TOXICOLOGICAL EVALUATION OF REALISTIC EMISSIONS OF SOURCE AEROSOLS (TERESA): APPLICATION TO POWER PLANT-DERIVED $PM_{2.5}$

Semi-Annual Technical Progress Report

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ABSTRACT

This report documents progress made on the subject project during the period of September 1, 2003 through February 28, 2004. The TERESA Study is designed to investigate the role played by specific emissions sources and components in the induction of adverse health effects by examining the relative toxicity of coal combustion and mobile source (gasoline and/or diesel engine) emissions and their oxidative products. The study involves on-site sampling, dilution, and aging of coal combustion emissions at three coal-fired power plants, as well as mobile source emissions, followed by animal exposures incorporating a number of toxicological endpoints. The DOE-EPRI Cooperative Agreement (henceforth referred to as “the Agreement”) for which this technical progress report has been prepared covers the analysis and interpretation of the field data collected at the first power plant (located in the Upper Midwest), followed by the performance and analysis of similar field experiments at two additional coal-fired power plants utilizing different coal types and with different plant configurations. Modifications to the original study design, which will improve the atmospheric aging component of the project and ensure that emissions are as realistic as possible, have resulted in project delays, and, at the time of report preparation, fieldwork at the Upper Midwest plant had not begun. However, such activities are imminent. This report therefore does not present data for activities covered by the Agreement, but does present results for the laboratory methods development work. This work is critical for the future success of the project. In particular, the atmospheric reaction simulation system is of paramount importance to the TERESA study design, since the basis for the toxicity assessment lies in the generation of realistic exposure atmospheres. The formation, composition, and toxicity of particles will be related to different atmospheric conditions and plume dilution scenarios through variations in reaction conditions. Because of the critical role played by this component in ensuring the overall success of the project, more time was required to develop and optimize the system, and the one-chamber simulation system outlined in the original Scope of Work for the Agreement was modified to comprise a more realistic dual chamber system. We are confident that the additional time required to optimize these methodologies will result in a significant improvement in the study. We fully expect that results for tasks covered under the Agreement, and a complete discussion of their relevance and value, will be included in the next semiannual progress report.

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INTRODUCTION

The TERESA study investigates the role played by specific emissions sources and components in the induction of adverse health effects by examining the relative toxicity of coal combustion and mobile source (gasoline and/or diesel engine) emissions and their oxidative products. The work is a significant improvement over previous studies to investigate the toxicity of coal combustion-derived particulate matter by virtue of several highly innovative and unique design features. First, all toxicological studies of coal combustion emissions to date (some of which have shown biological effects) have used primary emissions, ie. coal fly ash (e.g. MacFarland *et al*., 1971; Alarie *et al*., 1975; Raabe *et al*., 1982; Schreider *et al*., 1985). The relevance of primary emissions to human population exposure is unclear, since primary PM emissions are now very low with the widespread introduction of particulate controls on power plants. It is the secondary particulate matter formed from SO_2 and NO_x in stack emissions as well as any residual primary PM that is of interest. No efforts to consider and account for secondary atmospheric chemistry have been made to date. By examining aged, atmospherically transformed aerosol derived from stack emissions, TERESA will enable the determination of the toxicity of emissions sources in a manner that more accurately reflects the exposure of concern. In addition, the atmospheric simulation component of the project will allow us the investigations of the effect of different atmospheric conditions on the formation and toxicity of secondary PM. Second, the primary PM used in the studies to date has typically been generated through the use of pilot combustors in a laboratory setting. There is concern that pilot combustors may not accurately mimic stack emissions due to differences in surface to volume ratios and thus time-temperature histories. The fact that TERESA involves assessment of actual plant emissions in a field setting is an important strength of the study, since it eliminates any question of representativeness of emissions.

The study involves on-site sampling and dilution of coal combustion emissions at three coal-fired power plants, as well as mobile source emissions. Emissions are introduced into a reaction chamber to simulate oxidative atmospheric chemistry, and both primary and secondary materials are extensively characterized, including CO, NO_2, SO_2, ozone, NH_3, hydrocarbons, particle number and mass (including ultrafines), sulfate, nitrate, black/organic carbon (BC/OC), ammonium, and metals. Test atmospheres containing depleted emissions and emission oxidative products are utilized in two toxicological assessment steps, the first utilizing normal laboratory rats, and the second consisting of a comprehensive toxicological evaluation in a rat model of susceptible individuals. This last step includes telemetric methods for the assessment of cardiac function.

The primary objective of the project is to evaluate the potential for adverse health effects from ambient exposure to realistic coal-fired power plant emissions. Secondary objectives of the study include: (1) evaluate the relative toxicity of coal combustion emissions and mobile source emissions, their secondary products, and ambient particles; (2) provide insight into the effects of atmospheric conditions on the formation and toxicity of secondary particles from coal combustion and mobile source emissions through the simulation of multiple atmospheric conditions; (3) provide information on the impact of coal type and pollution control technologies on emissions toxicity; and (4) provide insight into toxicological mechanisms of PM-induced effects, particularly as they relate to susceptible subpopulations. The study findings will help to answer questions regarding which constituents of PM are responsible for the negative health outcomes observed, the likely sources of these constituents, and the degree to which further regulation of PM will improve human health.

The DOE-EPRI Cooperative Agreement for which this technical progress report has been prepared involves the analysis and interpretation of the field data collected at the first power plant (located in the Upper Midwest), followed by the performance and analysis of similar field experiments at two additional coal-fired power plants utilizing different coal types and with different plant configurations. The Agreement also includes a comparison of the toxicity of coal power plant emissions, mobile source emissions and concentrated ambient particles (CAPs). Animal exposure experiments to evaluate the toxicity of mobile source emissions and CAPs are also part of the overall TERESA program, but will be performed by the project team independently of the Agreement.

EXECUTIVE SUMMARY

Activities conducted during the first reporting period (September 1, 2003 through February 28, 2004) primarily focused on developing and finalizing the methodologies for the emissions aging component of the project, and preparing for fieldwork. Important accomplishments during this period include:

Technical Advisory Committee Activities:

- An interim teleconference of the TERESA Technical Advisory Committee was held on September 23, 2003. Discussions at this meeting and subsequent follow-up led to the development of the new approach to the atmospheric aging (described in more detail in the Experimental section).

Presentations/Papers:

- Rohr, A.C., Ruiz-Rudolph, P., Lawrence, J.E., Wolfson, J.M., and Koutrakis, P. Assessment of Aged Coal-Fired Power Plant Emissions: The TERESA Study. Presented at Air Quality IV, Arlington, VA, September 24, 2003.
- Rohr, A.C. Assessment of Secondary Coal Combustion Emissions. Presented at the Electric Utilities Environmental Conference, Tucson, AZ, January 22, 2004.

Sampling and Dilution System Development:

- A system was developed to deliver particle-free, dry compressed air to the venturi aspirator.
- Developed remote control of pressure for delivery of compressed air to the aspirator.
- Two different venturi aspirators were tested and calibrated.
- The venturi orifice was tested at different temperatures.
- 1" OD stainless steel transmission tubing was acquired to transfer diluted stack gas to the mobile chemical laboratory.
- Losses of ultrafine particles were characterized in the transmission tubing.
- A nozzle/flow restrictor was developed for transfer of diluted stack gas into the reaction chamber.
- An automated feedback control was developed to maintain constant flow into the reaction chamber.
- A field version of the dual-chamber atmospheric reaction simulation system was constructed.
- A system to transfer water mist into the reaction chamber was developed.
- A corrosion-resistant temperature/humidity probe and humidistat to control chamber humidity were installed.
- Field versions of the gas-cleaning devices (denuders) were constructed and tested.
- Sampling manifolds were constructed.
- A temperature/humidity-controlled air system to dilute flow out of the gas cleaner was developed.
- An automatic valve switching system to alternate input flow from different sampling manifolds to the continuous gas monitors was developed.
- A data acquisition system was designed and constructed.
- Systems for integrated sampling of particles and gases were designed and constructed.

Toxicological Lab Outfitting:

- Using laboratory hardware and research needs, a trailer floor plan and mechanical plan were developed.
- A trailer manufacturer and local vendor capable of building the mobile lab were selected.
- The trailer was prepared as a mobile lab.
- Ventilation addition was finalized.
- The lab was relocated to a nearby site (Framingham, MA) for initial operation.
- The lab was inspected by the Harvard Animal Resources Committee and approved for use.

Chemical Lab Outfitting:

- Using laboratory hardware and research needs, the bus floor plan and mechanical plan were developed.
- The reaction chamber and chamber enclosure were designed and constructed.
- Heat pumps, electric heaters, and the reaction chamber ventilation system were installed.
- The wiring plan was completed and installed.
- The reaction chamber and enclosure were completed, along with an instrument rack and worktable.

Planning for Remaining Host Plants:

- A. Rohr and Steve Ferguson (Harvard) visited a Southeast plant on March 11, 2004. The plant appears to be appropriate for study, and stack access was established.

EXPERIMENTAL

This section describes the revised simulated atmospheric reaction system, reaction chambers, gas-cleaning system, mobile laboratories, and stack gas sampling/dilution/transport system,

Revision of the Simulated Atmospheric Reaction Scheme

Feedback obtained during the Technical Advisory Committee teleconference in September 2003 and follow-up to this meeting was used to revise the scheme to simulate atmospheric reactions to produce secondary aerosol from the diluted stack gas. This revision is based on a more realistic two-stage model. This model assumes that the oxidation of SO_2 to form H_2SO_4 takes place primarily in the plume that is formed from the initial dispersion of the stack gas emission. The second stage occurs when the H_2SO_4 mixes with and is neutralized by ammonia from ground level sources, and where the neutralized or unneutralized sulfate particles also mix, independently, with VOCs from both anthropogenic and natural sources, and particle-phase organics are formed.

To perform the simulated reactions for the revised scheme, it is necessary to use two separate reaction chambers. In the first chamber, as in the original scheme, SO_2 is reacted with ozone and UV light to form H_2SO_4. Relatively high energy UV light will be used to produce sufficient hydroxyl radical concentrations to oxidize about 35% of the SO_2, resulting in a sulfate mass concentration of 2000 $\mu g/m^3$ for a residence time of about one hour. In the second reaction chamber, for one of the exposure scenarios, the acidic aerosol will be neutralized with ammonia, and for another exposure scenario, α-pinene (as a representative biogenic VOC) will be reacted with ozone to produce organic particulate matter. A significant advantage of the revised scheme is that the organic species are not exposed to high-energy UV light, so photochemical reactions that do not occur under normal atmospheric conditions are avoided.

Reaction Chambers

The final reaction chamber for the first stage has been constructed. The dimensions of this chamber are 152x122x30 cm, with a total volume of approximately 500L. The side (152x30 cm) and end (122x30 cm) surfaces of the chamber are made of opaque PTFE Teflon sheet. The larger 152x122 cm top and bottom surfaces are made of transparent PTFE Teflon film (in order to transmit UV irradiation). The chamber is designed to attach and detach the Teflon film easily, allowing periodic sheet replacement. Also, the chamber has wheels that facilitate its movement into and out of an enclosure that holds an array of UV lamps that face the two transparent Teflon film surfaces of the chamber.

A prototype reaction chamber for the second stage has been tested. The final field version has been constructed and is awaiting final modifications. This chamber has glass walls that are coated with Teflon lubricant to minimize wall reactions. The dimensions are 60x50x30 cm with a total volume of 90 L. At 5 LPM the residence time in the chamber is 18 minutes. This chamber was tested as a completely mixed flow reactor. Constant concentrations of ozone and pinene were added. Inside the chamber, pinene reacted with ozone and produced a concentration of 4000μg/m^3 of organic material (as measured by APS, SMPS and filter gravimetry). This concentration was stable over time and repetitive day after day.

A schematic of the new dual chamber reaction scheme is shown in Figure 1.

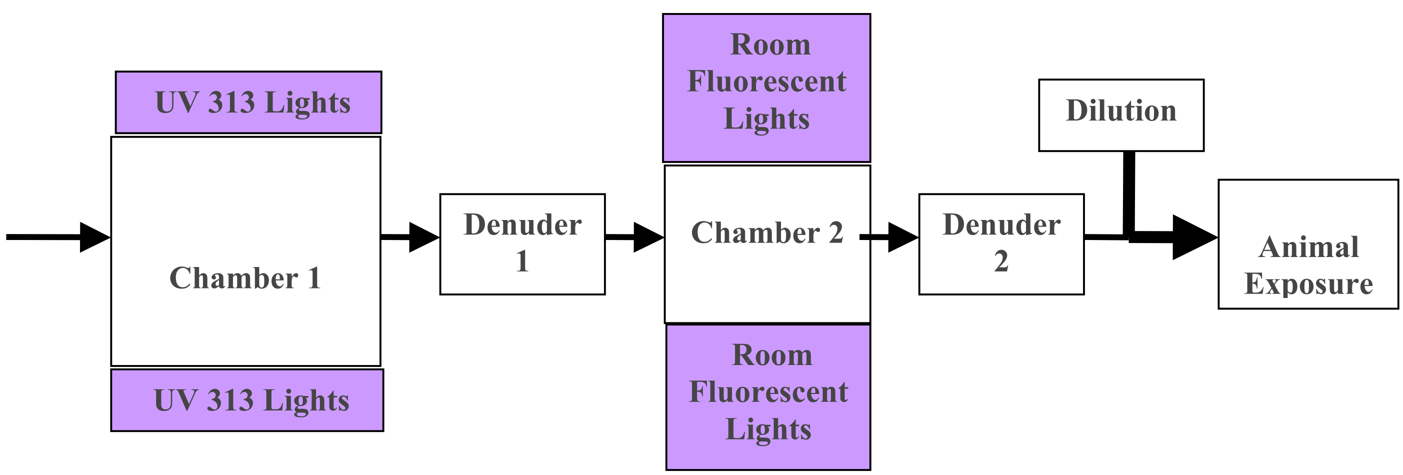

Figure 1. Dual Chamber System.

Removal of Excess Reactive Gases

Excess reactive gases will be removed from the first stage reaction mixture (while keeping the secondary particles suspended in air) using a gas cleaning system. The reaction mixture that is drawn out of the first stage reaction chamber passes through a counter-current diffusion denuder that removes 80-90% of the SO_2, NOx, and ozone. A second gas cleaning system is used downstream of the second stage reaction chamber to remove excess gas phase organics and ozone, as well as to further reduce the SO_2 and NOx concentrations prior to animal exposures. Final, field versions of both denuders have been constructed and tested. The mixture of secondary particles and reactive gases is drawn through an inner channel. Clean air is passed in a counter-flow fashion through two outer channels. Microporous PTFE Teflon membranes are placed between the inner and outer channels, which allow the diffusion of gaseous species, while particles pass through the denuder. A theoretical model has been derived, and performance has been evaluated with CO, SO_2, and SF_6 (which represent molecules with very different diffusion coefficients). Penetration values (fraction of the gas that passes through the denuder and does not pass out through the membrane) for various testing conditions are provided below in Table 1. These results show that penetration of SO_2 is 15% at a 2:2:1 flush ratio, while that of CO is 16% and 10% at flush ratios of 1:1:1 and 2:1:1, respectively, indicating that the denuder is performing as expected. Particle losses have been characterized and found to be constant as a function of size in the ultrafine fraction (~20-30%), while lower for larger size fractions.

Table 1. Denuder Performance.

1:1:1 Flush ratio @ 5LPM

Gas	Penetration	MW
CO	0.159	28.01
SF6	0.275	145.05

2:2:1 Flush ratio @ 5LPM

Gas	Penetration	MW
CO	0.098	28.01
SO2	0.150	64.06
SF6	0.223	146.05

Animal Exposure Facility

The interior of the trailer, including the alarm systems and added electrical systems, has been completed. Because a higher ventilation rate was needed, the trailer had to have a second electric service added to handle the larger heating requirement. This additional electrical capacity also provides more flexibility in the use of auxiliary equipment.

Electrical power was put in place to field test the mobile exposure laboratory at our pilot location in Framingham, MA; this field-testing has been completed and the laboratory is ready for deployment to the Upper Midwest field site. Notably, the Harvard Animal Resource Committee (ARC) has inspected the facility and has passed it for use in field studies using animals.

Buxco manifolds for animal exposures, flow controls, rotameters, and the new Buxco pump were acquired and tested. The second optical shutter system for the assessment of *in vivo* oxidative stress is complete. This newly designed system for use in the field studies has already had considerable laboratory testing of the first of these units and results are favorable.

Mobile Chemical Laboratory

It was necessary to complete the design and testing of the reaction chambers before completing the electrical wiring diagram for the mobile chemical lab. This has been done, and final installation of wiring has been completed. Heat pump compressors have been installed on the bus, along with an extended bumper and trailer hitch. The bus interior has been completed by TNE (the contractor), and includes HVAC and installation of furniture.

Stack Gas Sampling/Dilution/Transport System

We have purchased an optimum commercially available system to provide particle-free, dry pressurized clean air to be supplied to the sampling/dilution aspirator that simultaneously sucks the stack gas out and dilutes it. This system will function properly in both warmer and colder seasons. The compressor for this system has the additional advantage that it is vibration-free. This feature will help ensure safe operation when the entire system is installed high up from the ground near the stack gas port. We have also completed room temperature tests of the 2 LPM stainless steel venturi sampling orifice and characterization tests at stack gas temperatures (Figure 2). We acquired the optimal venturi aspirator (stainless steel) for dilution of the stack gas, and have performed flow vs pressure tests on two different models (Vacon JD250 and JD300) with the goal of determining optimum flexibility for the ratio of dilution air to stack gas. We also measured particle losses for artificial potassium sulfate aerosol during the process of collection through the venturi orifice and dilution in the JD 300 aspirator. The dilution ratio used was 88:1 (dilution flow to sample flow). The ratio of measured air concentrations of sulfate upstream and downstream agreed within experimental error with the known dilution ratio for the aspirator.

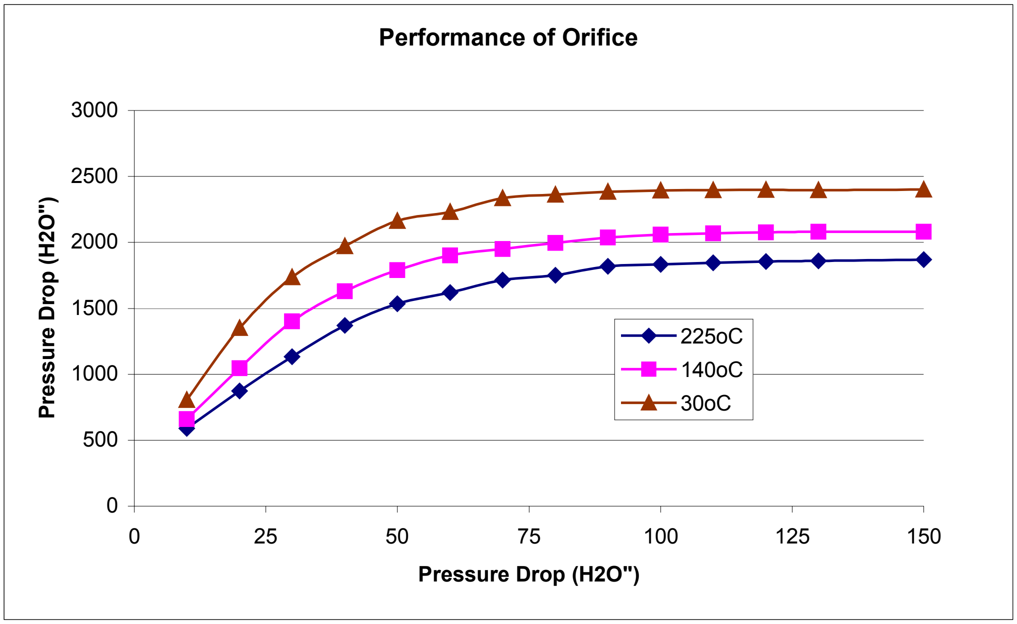

Figure 2. Venturi orifice performance at different temperatures.

Particle losses as a function of particle size were determined in the 1" OD stainless steel transmission tubing that carries the diluted stack gas from the aspirator on the stack duct to the mobile chemical laboratory. The smaller size range was measured using an SMPS (Scanning Mobility Particle Sizer) and the larger size range was measured using an APS (Aerodynamic Particle Sizer). Losses for the key size range, ultrafine particles, were negligible (Figure 3). Losses for the larger particles (Figure 4) increased with particle size, which is expected since impaction increases with momentum, which increases with size. The moderately small losses of the larger particles are not of great consequence for the design of this study, which depends primarily on the fate of the ultrafine particles in the growth of secondary pollutant aerosol.

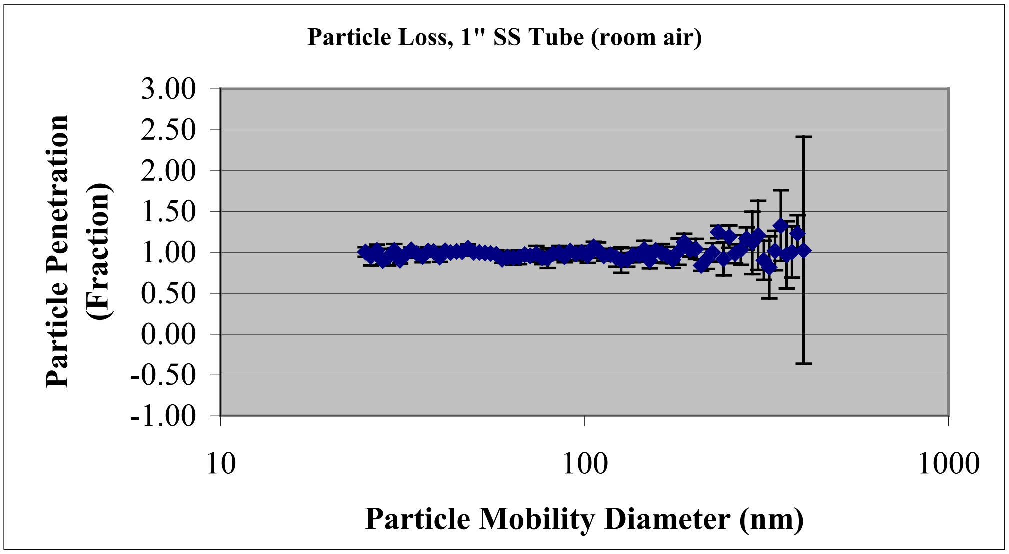

Figure 3. Ultrafine particle losses in transmission tubing.

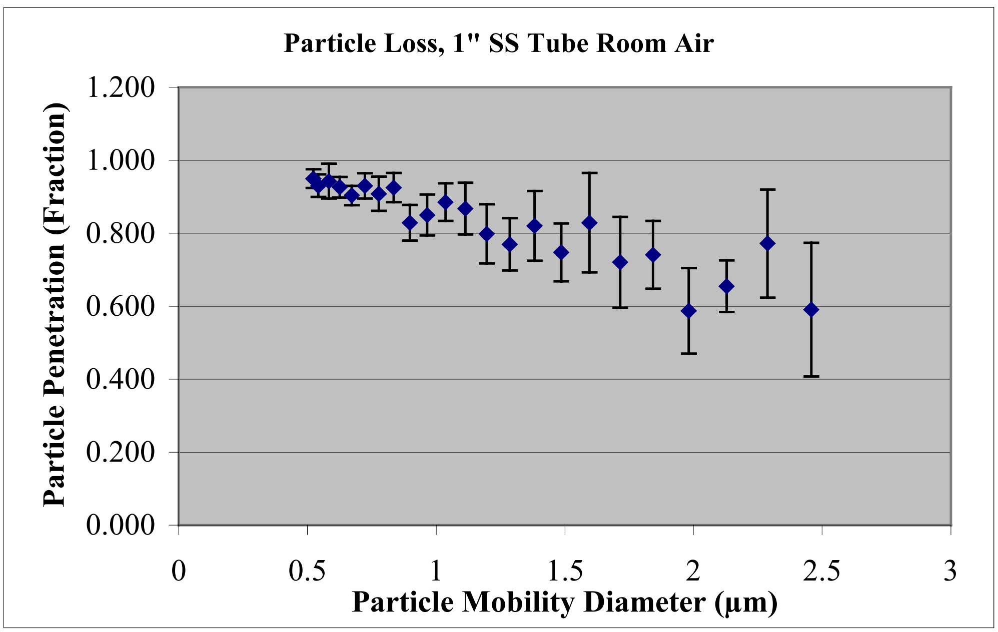

Figure 4. $PM_{2.5}$ losses in transmission tubing.

RESULTS AND DISCUSSION

We do not have results for the activities covered by the DOE-EPRI Cooperative Agreement at this time. We fully expect that such results, and a complete discussion of their relevance and value, will be included in the next semiannual progress report.

As such, the next reporting period (March 1, 2004 through August 31, 2004) will document the following activities:

- Construction and installation of the custom-built emissions collection/dilution/transmission system at a power plant in the Upper Midwest;
- Aging of the primary emissions from the Upper Midwest plant;
- Exposure of normal and compromised rats to emissions from the Upper Midwest plant subjected to different simulated atmospheric conditions;
- Physicochemical characterization of the exposure atmospheres at the Upper Midwest plant;
- Toxicological evaluation of the Upper Midwest scenario atmospheres;
- Detailed planning and preparation for Plant 1, located in the Southeastern U.S.

CONCLUSION

Although the project has been delayed, the value of the results will be enhanced, given the modifications that have been made to ensure that the system will produce emissions that are as realistic as possible. We are confident that the methodologies are sound and that fieldwork at the Upper Midwest plant will yield fruitful results.

A revised project schedule is provided on the following page. Below is a detailed schedule for the fieldwork to be carried out at the Upper Midwest plant. The plant will undergo a routine maintenance outage from May 15-30.

Schedule for Upper Midwest power plant fieldwork.

	M	T	W	T	F	S	Su
Set-Up/Test		13-Apr	14-Apr	15-Apr	16-Apr	17-Apr	18-Apr
Aerosol Testing	19-Apr	20-Apr	21-Apr	22-Apr	23-Apr	24-Apr	25-Apr
Normal Rats	26-Apr	27-Apr	28-Apr	29-Apr	30-Apr	1-May	2-May
Normal Rats	3-May	4-May	5-May	6-May	7-May	8-May	9-May
Normal Rats	10-May	11-May	12-May	13-May	14-May	15-May	16-May
PP Shut Down	17-May	18-May	19-May	20-May	21-May	22-May	23-May
PP Shut Down	24-May	25-May	26-May	27-May	28-May	29-May	30-May
Myocardial	31-May	1-Jun	2-Jun	3-Jun	4-Jun	5-Jun	6-Jun
Myocardial	7-Jun	8-Jun	9-Jun	10-Jun	11-Jun	12-Jun	13-Jun
Myocardial	14-Jun	15-Jun	16-Jun	17-Jun	18-Jun	19-Jun	20-Jun
Myocardial	21-Jun	22-Jun	23-Jun	24-Jun	25-Jun	26-Jun	27-Jun
Take Down	28-Jun	29-Jun	30-Jun	1-Jul	2-Jul	3-Jul	4-Jul

Project Performance Schedule

Months after Project Start: 2003: S O N D (1–4); 2004: J F M A M J J A S O N D (5–16); 2005: J F M A M J J A S O N D (17–28); 2006: J F M A M J J A S O N D (29–40)

Task	Subtask	Description
1		Complete Study at Upper Midwest Plant
	1.1	Laboratory Analysis of Air Quality Data
	1.2	Data Integration and Analysis
2		Field Study at Power Plant #1
	2.1	Stack Sampling/Dilution System
	2.2	Atmospheric Reaction Simulation System
	2.3	Animal Exposure Laboratory
	2.4	Toxicological Assessments
	2.5	Laboratory Analysis of Air Quality Data
	2.6	Data Integration and Analysis
3		Field Study at Power Plant #2
	3.1	Stack Sampling/Dilution System
	3.2	Atmospheric Reaction Simulation System
	3.3	Animal Exposure Laboratory
	3.4	Toxicological Assessments
	3.5	Laboratory Analysis of Air Quality Data
	3.6	Data Integration and Analysis
4		Relative Toxicity of Coal Plant and Mobile Source Emissions and CAPs
5		Preparation of Peer-Reviewed Journal Articles
6		Project Management and Reporting

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